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METHYL KETONES IN ROQUEFORT CHEESE

Quantitative analyses of the methyl ketones in commercial Blue and Camembert cheeses have been reported from this Laboratory (1, 2). In a continuing study of carbonyl compounds present in natural products, we have examined Roquefort cheese and present our results.

EXPERIMENTAL PROCEDURE

The cheeses were commercial brands aged, according to the label, a minimum of 60 days. For the analyses, 25 g of cheese were ground in a mortar with 25 g of Celite 545.[1] The powder was packed in a chromatography tube and the fat washed out with carbonyl-free hexane (3) until a total of 100 ml of effluent was collected. The effluent was then analyzed quantitatively for methyl ketones, using the procedures of Schwartz et al. (4).

RESULTS AND DISCUSSION

Results of the analyses are given in Table 1. As with Blue (1) and Camembert cheeses (2), the total concentration of ketone and the concentration of the individual ketones in Roquefort cheese varied markedly. One sample (Brand 2) contained more nonanone-2 than heptanone-2. This was the first *Penicillium roqueforti*-ripened cheese encountered in which heptanone-2 was not the predominant ketone.

Two observations made in the course of this work and our Blue cheese work which may deserve further attention are: (1) Removal of all monocarbonyls from the fat phase of the cheese does not eliminate the typical Blue- or Roquefort-type odor, and (2) Roquefort-cheese fat contains a nonvolatile carbonyl constituent in the monocarbonyl fraction in relatively high concentration, which is either absent or present in relatively very low concentration in Blue-cheese fat.

TABLE 1
Concentration of methyl ketones in Roquefort-cheese fat

Roquefort cheese	(C_{15} + C_{13})	C_{11}	C_9	C_7	C_5	C_3
	μM per 10 g of extracted fat					
Brand 1	0.5	0.7	7.4	15.6	11.0	2.4
Brand 2	0.4	1.6	12.9	9.2	1.2	0.0
Brand 3	0.3	0.3	2.6	4.2	0.0	0.0

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[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

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HYDROLYSIS OF THE TRIGLYCERIDES OF BUTTER BY PANCREATIC LIPASE. LOCATION OF BUTYRIC ACID

Volatile acids were steam-distilled into aqueous sodium carbonate solution and the resulting soaps dried with a large excess of absolute alcohol and butylated directly in the same flask (2). Analysis of the butyl esters of the different fractions was performed at two different temperatures with a Barber-Colman Model 10 gas chromatographic apparatus by the method of Clément and Bezard (2). In experiments of 20 min duration the extent of hydrolysis for all glyceride fractions was between 50 and 55%.

The three triglyceride fractions (Table 1) of butter originally contained the same types of fatty acids, but were distinguished by different proportions of the short-chain acids. After lipolysis, certain changes in the composition of the remaining triglycerides are noteworthy. These can be interpreted only in terms of preferential attack on the substrates containing the short-chain acids. Thus, the principal difference among the three types of monoglycerides, MG_1, MG_2, and MG_3, is concerned with their content of butyric acid: MG_2 and MG_3 contained none, despite the fact that the triglycerides from which they were derived, T_2 and T_3, contained 75% of the total amount of this acid. Moreover, all the butyric acid was found in the liberated fatty acids (see Table 1).

It must, therefore, be concluded, on the strength of experiments involving synthetic mixtures (1), that triglycerides T_2 and T_3 contain no butyric acid in the β position and, conversely, that 75% of the butyric acid of the triglycerides of butter is in the α positions. It will be seen that the monoglyceride, MG_1 retained a considerable proportion of butyric acid, but from our experiments with synthetic substrates, it would be difficult to determine the original position of the liberated butyric acid. We have confirmed by gas chromatography that fraction T_1 contains no tributyrin, in agreement with previous work (3, 6).

TABLE 1

Composition of fatty acids (molar percentages) of the triglycerides of butter before and after lipolysis, the monoglycerides and the liberated free fatty acids

No. of carbon atoms of the fatty acids	C_4	$C_6 + C_8$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$
Triglycerides T_1[a]	2.4	3.79	2.8	2.8	8.5	20.6	10.4	27.1	4.0
Triglycerides T_1[b]	4.7	3.37	Traces	Traces	8.8	24.4	11.3	27.9	2.7
Monoglycerides MG_1	5.4	3.60	2.8	2.5	13.4	28.3	7.3	23.0	2.7
Free fatty acids AG_1	10.1	3.14	1.2	2.9	9.5	19.5	5.2	25.42	3.3
Triglycerides T_2[a]	16.6	7.54	2.0	3.0	10.7	22.3	7.7	19.2	1.8
Triglycerides T_2[b]	4.6	2.16	2.5	2.9	10.4	31.4	10.7	23.3	2.3
Monoglycerides MG_2	0	2.05	3.8	5.1	20.2	34.1	4.0	12.2	1.3
Tdiglycerides T_3[a]	16.1	5.31	1.0	3.7	12.0	23.3	5.3	19.8	2.8
Triglycerides T_3[b]	19.2	3.01	Traces	7.3	12.4	20.6	3.4	17.9	3.2
Monoglycerides MG_3	0	3.07	2.5	4.4	10.3	21.7	4.8	14.8	3.6
Free fatty acids AG_3	35.9	6.70	1.4	14.5	6.1	12.7	1.3	12.7	2.9

[a] Before lipolysis.
[b] After lipolysis.

In calculating the molar percentages we considered all the fatty acids obtained, whether identified or not, but only the principal ones were included in the table.

In summary, it can be concluded that at least 75% of the butyric acid of butter is situated in the α positions of the triglycerides. As for the remaining 25%, it is not possible at present to give its percentage distribution between Positions 2 and 1-3, although it seems very likely that some butyric acid is situated in Position 2, contrary to the opinion of Kumar et al. (5), but in agreement with the recent findings of Jensen and Gander (4) for milk glycerides.

It is possible that with even finer chromato-